Equivalent multipole operators for degenerate Rydberg states

V. N. Ostrovsky
V. Fock Institute of Physics, St. Petersburg State University, 198904 St. Petersburg, Russia

D. Vrinceanu
Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

M. R. Flannery
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332, USA
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As shown by Pauli, [Z. Phys. **36**, 336 (1926)], the electric dipole operator **r** can be replaced by the Runge-Lenz vector **A** when operating within the n^2 degenerate manifold of hydrogenic states of principal quantum number n. We seek to develop similar rules for higher multipole operators by expressing equivalent operators in terms only of the two vector constants of motion—the orbital angular momentum **L** and the Runge-Lenz vector **A**—appropriate to the degenerate hydrogenic shell. Equivalence of two operators means here that they yield identical matrix elements within a subspace of Hilbert space that corresponds to fixed n. Such equivalent-operator techniques permit direct algebraic calculation of perturbations of Rydberg atoms by external fields and often exact analytical results for transition probabilities. Explicit expressions for equivalent quadrupole and octupole operators are derived, examples are provided, and general aspects of the problem are discussed.

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I. INTRODUCTION

Highly excited Rydberg states with the same principal quantum number n have small deviations from pure hydrogenic behavior. The degenerate shell of these states forms the basis of a representation of the O(4) symmetry group [1] associated with the $1/r$ Coulomb potential governing the dynamics of the Rydberg electron. Many structural properties of the Rydberg atom can then be calculated by using algebraic rules and group representation techniques. These features combine mathematical beauty with pragmatic usefulness. Moreover, such algebraic techniques facilitate direct quantal and classical solution of Rydberg atoms in static external electric and magnetic fields [2], slow collisions with Rydberg atoms [3–5], and intrashell dynamics of a Rydberg atom in time-dependent electric and magnetic fields [6]. For example, analytical probabilities have been derived [3–5], without the need for any perturbative and numerical analysis, for the full array of $l \rightarrow l'$ transitions in atomic hydrogen $H(nl)$ induced by a time-varying weak electric field generated by adiabatic collision with slow ions.

The dimension of the degenerate subspace grows as n^2 (without electron spin) and traditional close-coupling (R-matrix) calculations using spatial wave functions become prohibitively difficult and ultimately impractical, either because of the sheer dimension of the space or because of the large number of oscillations. Rydberg states with n as large as several hundred are now accessible to observations and experiments. The group representation technique may therefore offer the only practical and effective way of solving problems involving such Rydberg states. In so doing, some essential underlying physics can be exposed, as an additional asset.

In particular, the theory of a Rydberg atom in weak external electric and magnetic fields is reduced to an algebraic problem that is extremely well poised towards extracting both quantitative analytical results and qualitative insight. This is possible provided the necessary operators of interaction with the fields can be represented in terms of integrals of motion—the angular momentum operator **L** (common to all central field problems) and the Runge-Lenz vector **A** (specific to the Coulomb potential alone). This key step, basic to the subsequent algebraic construction, can be only taken when the dynamics becomes restricted to the subspace of energy degenerate states, i.e., when the external perturbation is so weak that it does not induce n-n' coupling among shells of different energy.

All of the above work [2–6] was based on a paper as old as quantum mechanics [7]. There, Pauli [7] has shown that the electric dipole operator **r** becomes identical with the Runge-Lenz vector when the two operators are restricted to an energy shell with fixed principal quantum number n. This can most easily be seen by comparing all the matrix elements of these operators between states within the same energy shell. The power of this result comes from its general validity and utility for any shell with quantum number n.

The advantage of expressing the intrashell dynamics of Rydberg atoms in terms of the **A**,**L** set of constants for electronic Coulombic motion has already been demonstrated [3–5] for collisional l mixing transitions induced by a projectile charge-Rydberg dipole interaction. Also the interaction between two Stark-stretched (polar) Rydberg atoms has recently been expressed [8] in terms of interactions between the permanent multipoles of each atom. A basic question now arises quite naturally from these studies [3–5,8]. It is one which does not appear to have been previously posed or addressed. *Can all higher multipole interactions be equivalently expressed solely in terms of the* **A**,**L** *integrals of motion on the energy shell?*

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In an effort to answer this, the present paper considers general equivalent multipole operators in Secs. II and III. A procedure is then presented and applied, with examples, to the explicit determination in Secs. IV, V, and VI of the equivalent operators for the dipole, quadrupole, and octupole moments, respectively. The algebraic evaluation of the operators in terms of $(\mathbf{A},\mathbf{L})$ is conducted in the Appendixes. Our eventual aim is to provide, if possible, the full solution for general multipoles. Atomic units are used throughout the paper, unless otherwise noted.

II. INTRASHELL EQUIVALENT OPERATORS

The angular momentum $\mathbf{L}$ and the unrestricted Runge-Lenz vector

$$\mathbf{U} = \frac{1}{2}(\mathbf{p}\times\mathbf{L} - \mathbf{L}\times\mathbf{p}) - \frac{\mathbf{r}}{r}$$

are constants of motion for the internal Hamiltonian $H = p^2/2 - 1/r$ of the Rydberg atom. A more convenient form for the unrestricted Runge-Lenz vector is

$$\mathbf{U} = \frac{1}{2}\mathbf{r}p^2 - \mathbf{p}(\mathbf{r}\cdot\mathbf{p}) + \mathbf{r}H.$$

The vector operators $\mathbf{L}$ and $\mathbf{U}$ do not close under commutation to form a Lie algebra because

$$[U_i, U_j] = (-2H)i\epsilon_{ijk}L_k,$$

where ϵ_{ijk} is the Levi-Civita antisymmetric symbol for indices $i,j,k=1,2,3$. If, however, the action of operators $\mathbf{U}$ is restricted to the Hilbert subspace of states with principal quantum number n, then the Runge-Lenz vector for bound states of energy E_n can be defined as

$$\mathbf{A} = \frac{1}{\sqrt{-2E_n}}\left[\frac{1}{2}\mathbf{r}p^2 - \mathbf{p}(\mathbf{r}\cdot\mathbf{p}) + \mathbf{r}E_n\right]. \tag{1}$$

The six components of the vector operators $\mathbf{A}$ and $\mathbf{L}$ are generators of the symmetry group SO(4) of proper rotation in four dimensions. They satisfy the commutation relations $[A_i,A_j]=i\epsilon_{ijk}L_k$, $[L_i,L_j]=i\epsilon_{ijk}L_k$ and $[L_i,A_j]=i\epsilon_{ijk}A_k$. The discrete part of the hydrogenic spectrum is then exhibited [7] by the theory of irreducible representations of SO(4).

When redefined by Eq. (1), the Runge-Lenz vector $\mathbf{A}$ acts only on states within the n shell and has nonzero matrix elements only between states within the n shell. If P_n is the projector onto the n-shell subspace then one can write

$$\mathbf{A} = P_n\frac{\mathbf{U}}{\sqrt{-2H}}P_n.$$

The operators $\mathbf{A}$ and $\mathbf{U}/\sqrt{-2H}$ are equivalent because all their matrix elements are equal when evaluated between all states within the same n shell. In general, the operators $\mathcal{A}$ and $\mathcal{B}$ are equivalent within the n shell if all their intrashell matrix elements are equal

$$\langle n\gamma|\mathcal{A}|n\gamma'\rangle = \langle n\gamma|\mathcal{B}|n\gamma'\rangle. \tag{2}$$

The quantum numbers γ label the basis set which spans the n^2 degenerate subspace. Spherical (n,l,m), parabolic (n_1,n_2,m), Stark (n,k,m) or algebraic (n,m_1,m_2) quantum numbers are all useful hydrogenic sets (see, e.g., Ref. [8], Table 1). When an operator has an n-shell equivalent which can be expressed in terms of the constants of motion $\mathbf{L}$ and $\mathbf{A}$, then its intrashell matrix elements are easily calculated in any basis of states, using the SO(4) irreducible matrix representations. For example, Pauli [7] has proven that

$$P_n\mathbf{r}P_n = -\frac{3n}{2}\mathbf{A},$$

so that the dipole operator $\mathbf{r}$ within the n shell is equivalent to $-(3n/2)\mathbf{A}$. The dipole matrix elements between all (l,m) states of the same n are therefore simply related to the matrix elements of $\mathbf{A}$, which are then algebraically determined most effectively in the algebraic or Stark bases.

III. MULTIPOLE AND MULTIPOLE-TYPE OPERATORS

Many applications require calculation of matrix elements of higher multipole operators and therefore it is useful to find their n-shell equivalents. The spherical-coordinate representation of the multipole operator of order λ is

$$Q_\mu^{(\lambda)} = \sqrt{\frac{4\pi}{2\lambda+1}}r^\lambda Y_{\lambda\mu}(\hat{\mathbf{r}}), \tag{3}$$

where $\mathbf{r}$ is the electron position vector, with magnitude r and direction $\hat{\mathbf{r}}$, and where μ are the $2\lambda+1$ components with $-\lambda\le\mu\le\lambda$. Equation (3) for $\lambda=1,2,3$ provides the dipole, quadrupole, and octupole operators, respectively. In general, as a function of coordinates, the multipole $Q_\mu^{(\lambda)}$ is a solution of the Laplace equation in the entire free space (excluding the singular $\mathbf{r}=0$ point).

Another definition [9], which directly reveals the irreducible tensor properties of the multipole operators, is

$$Q_\mu^{(\lambda)} = \sqrt{\frac{(2\lambda-1)!!}{\lambda!}}\{\cdots\{\{\mathbf{r}\otimes\mathbf{r}\}^{(2)}\otimes\mathbf{r}\}^{(3)}\cdots\otimes\mathbf{r}\}_\mu^{(\lambda)}, \tag{4}$$

which represents Q as a multiple irreducible tensor product of vector $\mathbf{r}$ over itself λ times. A multipole-type operator is obtained if the identical factors $\mathbf{r}$ are replaced by different vectors $\mathbf{a},\mathbf{b},\mathbf{c},\ldots$. Theory based on this definition will not be developed here but will be the subject of future investigation.

Representation of the multipole operator by its Cartesian components provides several advantages for the approach taken in the present paper. The tensor $q^{(\lambda)}$ of rank λ with Cartesian components

$$q_{i_1i_2\cdots i_\lambda} = \frac{(-1)^\lambda r^{2\lambda+1}}{(2\lambda-1)!!}\partial_{i_1}\partial_{i_2}\cdots\partial_{i_\lambda}\frac{1}{r} \tag{5}$$

is a harmonic polynomial of power λ in the Cartesian components x_j $(j=1,2,3)$ of the electronic position vector $\mathbf{r}$. Harmonic polynomials, by definition, satisfy the Laplace equation. For $\lambda>1$, the tensor (5) can be expanded as a sum of terms, as a result of taking successive derivatives. One of the terms is $x_{i_1},x_{i_2},\ldots,x_{i_\lambda}$, while the remaining terms contain at least one Kronecker delta symbol for a pair of indices. However, not all 3^λ components of the tensor $q^{(\lambda)}$ are inde-

pendent because the tensor is fully symmetrical with regard to index permutation and has zero trace when any pair of indices is contracted. The fully symmetric tensor has $\binom{\lambda+2}{\lambda}$ independent components and there are $\binom{\lambda}{2}$ pairs of indices for which the trace is zero. The tensor $q^{(\lambda)}$ has therefore only $\binom{\lambda+2}{\lambda}-\binom{\lambda}{2}=2\lambda+1$ independent components. The first three multipole operators have the following Cartesian components:

$$q_i^{(1)} = x_i, \tag{6}$$

$$q_{ij}^{(2)} = x_i x_j - \frac{1}{3} r^2 \delta_{ij}, \tag{7}$$

$$q_{ijk}^{(3)} = x_i x_j x_k - \frac{1}{5} r^2 (x_i \delta_{jk} + x_j \delta_{ik} + r_k \delta_{ij}), \tag{8}$$

for the dipole, quadrupole, and octupole moments, respectively. An alternative definition for the Cartesian components (5) is obtained by starting from the monomial $x_{i_1}, x_{i_1}, \ldots, x_{i_\lambda}$ and constructing from it the tensor components $q_{i_1,i_2,\ldots,i_\lambda}$ by adding terms such that the result has both the required symmetry and the zero trace condition for all pairs of indices. As an example, the octupole operator is explicitly derived via this procedure in Sec. VI. This is also the way one can construct *multipole-type* operators starting from a set of vectors ($\mathbf{L}$ and $\mathbf{A}$ in our present case) which replace the position vector. For example, if one begins with vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}, \ldots$, the multipole-type operator contains the Cartesian components $a_{i_1}, b_{i_2}, c_{i_3}, \ldots$, and the remaining terms are obtained by permutations and contractions. Care must, however, be exercised when the operators do not commute.

A relation between the spherical (3) and Cartesian (5) components of the multipole operator is facilitated by using the following definition for the spherical harmonics:

$$Y_{LM}(\hat{\mathbf{r}}) = (-1)^{L-M} r^l \left(\frac{2L+1}{4\pi (L+M)!(L-M)!} \right)^{1/2} \times (\partial_1 + i\partial_2)^M \partial_3^{L-M} \frac{1}{r},$$

so that

$$Q_M^{(L)} = \frac{(-1)^M (2L-1)!!}{[(L+M)!(L-M)!]^{1/2}} \sum_{k=0}^{M} i^k \binom{M}{k} q_{\underbrace{1\cdots1}_{M-k}\underbrace{2\cdots2}_{k}\underbrace{3\cdots3}_{L-M}}$$

provides the required result. Explicit relations are

$$Q_0^{(1)} = q_3^{(1)},$$

$$Q_1^{(1)} = -(q_1^{(1)} + i q_2^{(1)})/\sqrt{2}, \tag{9}$$

for the dipole operator,

$$Q_0^{(2)} = \frac{3}{2} q_{33}^{(2)},$$

$$Q_1^{(2)} = -\sqrt{\frac{3}{2}} (q_{13}^{(2)} + i q_{23}^{(2)}),$$

$$Q_2^{(2)} = \frac{1}{2} \sqrt{\frac{3}{2}} (q_{11}^{(2)} + 2i q_{12}^{(2)} - q_{22}^{(2)}), \tag{10}$$

for the quadrupole operator and

$$Q_0^{(3)} = \frac{5}{2} q_{333}^{(3)},$$

$$Q_1^{(3)} = -\frac{5}{4} \sqrt{3} (q_{133}^{(3)} + i q_{233}^{(3)}),$$

$$Q_2^{(3)} = \frac{1}{2} \sqrt{\frac{15}{2}} (q_{113}^{(3)} + 2 q_{123}^{(3)} - q_{223}^{(3)}),$$

$$Q_3^{(3)} = -\frac{1}{4} \sqrt{5} (q_{111}^{(3)} + 3i q_{112}^{(3)} - 3 q_{122}^{(3)} - i q_{222}^{(3)}) \tag{11}$$

for the octupole operator. We now seek to obtain equivalent multipole operators within the n shell by constructing general multipole-type operators

$$P_n Q^{(\lambda)} P_n = \mathcal{F}^{(\lambda)}(\mathbf{L}, \mathbf{A})$$

from the two vector constants of motion $\mathbf{L}$ and $\mathbf{A}$. Because the multipole operator $Q^{(\lambda)}$ of order λ is a uniform function of coordinates of order λ, coordinate scaling $\mathbf{r} \to \gamma \mathbf{r}$ implies that the operator scales as $Q^{(\lambda)} \to \gamma^\lambda Q^{(\lambda)}$. We therefore require a similar property for the equivalent operator, such that $\mathcal{F}$ contains products of λ terms, where each of them can be either $\mathbf{L}$ or $\mathbf{A}$. Further restrictions follow from parity (coordinate-inversion) considerations—the parity of $Q^{(\lambda)}$ is $(-1)^\lambda$, the parity of $\mathbf{A}$ is -1, and the parity of $\mathbf{L}$ is $+1$. Multipoles of even order may therefore contain only products of even number of $\mathbf{L}$ operators. The equivalent dipole operator (with odd parity) is expressed only in terms of $\mathbf{A}$. The equivalent quadrupole operator (even-parity) has terms $\mathbf{A}\cdot\mathbf{A}$ and $\mathbf{L}\cdot\mathbf{L}$, but not the odd-parity terms with $\mathbf{A}\cdot\mathbf{L}$. Because of parity considerations, the equivalent octupole operator can only contain the two odd-parity terms, $\mathbf{A}\cdot\mathbf{A}\cdot\mathbf{A}$ and $\mathbf{A}\cdot\mathbf{L}\cdot\mathbf{L}$, while the even-parity term $\mathbf{A}\cdot\mathbf{A}\cdot\mathbf{L}$ is forbidden.

IV. EQUIVALENT DIPOLE OPERATOR

Using the general procedure outlined in the previous section, we seek the operator equivalent to the dipole operator (6) in the form

$$P_n q^{(1)} P_n = P_n \mathbf{r} P_n = a\mathbf{A} + b\mathbf{L}.$$

The operator $\mathbf{L}$ has the opposite parity of $q^{(1)}$ and is therefore precluded by setting $b=0$. The coefficient a is calculated by comparing the matrix elements of $\mathbf{A}$ and $\mathbf{r}$. Because of identical rotation properties of the two vectors, it is sufficient to calculate the matrix elements only along one direction. It is convenient to choose this direction as the z direction. Because of the selection rules, the dipole operator $\mathbf{r}$ and the Runge-Lenz vector $\mathbf{A}$ have nonzero matrix elements only between states with angular momentum quantum numbers differing by one unit ($l' = l \pm 1$).

Using Eq. (9), the intrashell matrix elements of the z component of the dipole are

$$\langle nl-1m|z|nlm\rangle = (R_{nl-1}|r|R_{nl})(Y_{l-1m}|Y_{10}|Y_{lm}) = -\frac{3}{2}n\sqrt{\frac{(n^2-l^2)(l^2-m^2)}{(2l-1)(2l+1)}}, \quad (12)$$

where the results (A3) and (A11) of Appendix A have been used.

On the other hand, the Runge-Lenz component A_z has the matrix elements

$$\langle nl-1m|A_z|nlm\rangle = \sqrt{\frac{(n^2-l^2)(l^2-m^2)}{(2l-1)(2l+1)}}, \quad (13)$$

easily deduced from Eq. (A17).

By comparing Eqs. (12) and (13), the coefficient is $a=-3n/2$. This reproduces, as expected, the result $\mathbf{r}\to-(3n/2)\mathbf{A}$ originally obtained by Pauli [7]. The position operator $\mathbf{r}$ can be therefore replaced by the Runge-Lenz vector, when restricted to states within the n shell. This result is sometimes referred to as "Pauli's replacement rule," which, in addition to Pauli's original proof [7] can also be derived from other approaches, as in Refs. [2,3]. It is useful to note that the Cartesian components commute when unrestricted ($[x,y]=0$, for example), but behave as angular momentum vectors when restricted to the n shell, because $[A_x,A_y]=iL_z$.

V. EQUIVALENT QUADRUPOLE OPERATOR

The quadrupole operator is a rank 2 tensor with Cartesian components q_{ik} defined by Eq. (7). It is symmetrical ($q_{ik}=q_{ki}$) and has zero trace ($\Sigma_i q_{ii}=0$). Two quadrupolelike operators, symmetrical, with zero trace and even parity, can be constructed from $\mathbf{A}$ and $\mathbf{L}$ and can contribute to the equivalent quadrupole operator. They are

$$O_{ij}^{(1)} = \frac{1}{2}(A_iA_j + A_jA_i) - \frac{1}{3}A^2\delta_{ij} \quad (14)$$

and

$$O_{ij}^{(2)} = \frac{1}{2}(L_iL_j + L_jL_i) - \frac{1}{3}L^2\delta_{ij}, \quad (15)$$

where the end δ_{ij} term insures zero trace. Mixed terms of the form A_iL_j have odd parity (sign changes under coordinate inversion) and are therefore precluded. The equivalent quadrupole operator has therefore the general form

$$P_n q^{(2)} P_n = aO^{(1)} + bO^{(2)},$$

where the coefficients a and b are determined by comparing the matrix elements of specific tensor components, between states with angular momentum quantum number differing by 0 or 2 units, i.e., ($l'=l,l\pm2$).

It is convenient to calculate the matrix elements of the zz, or 33, components of the quadrupole and quadrupolelike operators and then to solve the set of equations

$$\langle nlm|q_{33}^{(2)}|nlm\rangle = a\langle nlm|O_{33}^{(1)}|nlm\rangle + b\langle nlm|O_{33}^{(2)}|nlm\rangle,$$

$$\langle nl'm|q_{33}^{(2)}|nlm\rangle = a\langle nl'm|O_{33}^{(1)}|nlm\rangle + b\langle nl'm|O_{33}^{(2)}|nlm\rangle$$

for the coefficients a and b, where $l'=l-2$.

A. Implementation

Explicit calculations of the above matrix elements of $q_{33}^{(2)}$, $O_{33}^{(1)}$, and $O_{33}^{(2)}$ yield the results (A20), (A21), (A24), and (A23), derived in Appendix A. The coefficients are thus calculated as $a=5n^2/2$ and $b=-n^2/2$. The quadrupole equivalent operator can therefore be expressed exclusively in terms of the $\mathbf{L}$ and $\mathbf{A}$ operators as

$$P_n q_{ij}^{(2)} P_n \equiv P_n\left(x_ix_j - \frac{1}{3}r^2\delta_{ij}\right)P_n = \frac{5n^2}{4}\left(A_iA_j + A_jA_i - \frac{2}{3}A^2\delta_{ij}\right) - \frac{n^2}{4}\left(L_iL_j + L_jL_i - \frac{2}{3}L^2\delta_{ij}\right). \quad (16)$$

This is our desired rule which replaces the Cartesian quadrupole components (7) by Eq. (16). From this general rule, the equivalent-operator relation

$$\rho^2 \equiv x^2 + y^2 = r^2 - z^2 = \frac{n^2}{2}(n^2 + 3 + L_z^2 + 4A^2 - 5A_z^2), \quad (17)$$

for the cylindrical diagonal element squared is readily deduced. Expression (17), originally proven by Solov'ev [10], was key to theoretical development for the hydrogen atom in weak magnetic fields and in crossed electric and magnetic fields (see Ref. [11], for example). The explicit rule (16) provides, of course, all five independent quadrupole tensor elements.

B. Equivalent operator for $nlm\to nlm'$ transitions

It is worth noting that a construction was developed earlier for the 3D rotational SO(3) group with generator $\mathbf{L}$ and the *unit* vector $\mathbf{n}=\mathbf{r}/r$, instead of the SO(4) group vector $\mathbf{r}$. In one of their problems [13], Landau and Lifshitz derive the equivalent-operator relation

$$n_in_k - \frac{1}{3}\delta_{ik} = -\frac{1}{(2l-1)(2l+3)}\left[L_iL_k + L_kL_i - \frac{2}{3}L^2\delta_{ik}\right] \quad (18)$$

to be compared with our equivalent operator (16). This relation (18) is valid for the Hilbert space of states on a unit sphere, within the subspace of states with definite total angular momentum l (but with different m), i.e., for $nlm\to nlm'$ transitions. The definition of equivalent operators for this SO(3) group is

$$\langle nl\gamma|\mathcal{A}|nl\gamma'\rangle = \langle nl\gamma|\mathcal{B}|nl\gamma'\rangle \quad (19)$$

in contrast to the definition (2) of hydrogenic SO(4) equivalent operators. The present study provides the multipole operators, i.e., irreducible tensors built from electron coordinate

r, in terms of the hydrogenic SO(4) symmetry group generators **L** and **A** which permit all intrashell $nlm \to nl'm'$ transitions.

C. Quadrupole operator in the SO(3)⊗SO(3) representation

In the Coulomb problem, it is conventional to replace **L** and **A** by a pair of integrals of motion $\mathbf{I}^{(1)}$ and $\mathbf{I}^{(2)}$ related by

$$\mathbf{I}^{(1)} = \frac{1}{2}(\mathbf{L}+\mathbf{A}), \quad \mathbf{I}^{(2)} = \frac{1}{2}(\mathbf{L}-\mathbf{A}),$$

$$\mathbf{L} = \mathbf{I}^{(1)} + \mathbf{I}^{(2)}, \quad \mathbf{A} = \mathbf{I}^{(1)} - \mathbf{I}^{(2)}.$$

The operators $\mathbf{I}^{(1)}$ and $\mathbf{I}^{(2)}$ possess all the properties enjoyed by *independent* angular momentum quantum-mechanical operators

$$(\mathbf{I}^{(1)})^2 = (\mathbf{I}^{(2)})^2 = j(j+1), \quad j = \frac{1}{2}(n-1),$$

$$[\mathbf{I}^{(1)},\mathbf{I}^{(2)}] = 0.$$

These pseudospin operators are generators of SO(3) ⊗SO(3) representation of algebra of SO(4) symmetry group in quantum mechanics and provide the algebraic basis set [8] of wave functions with quantum numbers (n,m_1,m_2). The equivalent quadrupole operator rule (16) can now be recast in terms of pseudospin vectors $\mathbf{I}^{(1)}$ and $\mathbf{I}^{(2)}$ as

$$\begin{aligned} q_{ik}^{(2)} &= n^2[I_i^{(1)}I_k^{(1)} + I_k^{(1)}I_i^{(1)} + I_i^{(2)}I_k^{(2)} + I_k^{(2)}I_i^{(2)}] \\ &\quad - 3n^2[I_i^{(1)}I_k^{(2)} + I_i^{(2)}I_k^{(1)}] - \frac{1}{3}n^2(n^2-1)\delta_{ik} \\ &\quad + 2n^2[\mathbf{I}^{(1)}\cdot\mathbf{I}^{(2)}]\delta_{ik}. \end{aligned}$$

D. Application: Averaged ion-quadrupole interaction

In a number of physical problems, the angular momenta operators $\mathbf{I}^{(1)}$ and $\mathbf{I}^{(2)}$ are quantized with respect to independent axes $\boldsymbol{\omega}_1$ and $\boldsymbol{\omega}_2$ in space. One example is the hydrogen atom in crossed electric and magnetic fields, where the vectors $\boldsymbol{\omega}_1$ and $\boldsymbol{\omega}_2$ are expressed [2] in terms of the electric field strength and the magnetic field induction. This approach is extended also to time-dependent fields [6]. Another example appears in the theory [3,5] of intrashell mixing in excited hydrogen atom by collision with a particle with charge Z_B. Here, in the corotating frame, the electric field is space-fixed and directed along the z axis towards charge Z_B, while the effective magnetic field is perpendicular to it and normal to the collision plane. The theory [3,5] of intrashell mixing usually accounts only for the leading and dominant charge-dipole term in the expansion for the full charge (Z_B)-Rydberg atom interaction. The next term is the charge-quadrupole interaction which, in the corotating frame, is

$$3Z_B\frac{q_{33}^{(2)}}{R^3}, \tag{20}$$

where **R** is a vector directed from the atomic nucleus of the target atom towards the projectile of charge Z_B and the component along **R** is denoted by subscript 3.

As a useful application of the present equivalent-operator method, we evaluate the average of interaction (20) appropriate to perturbation theory. Namely, we perform in the SO(3) ⊗ SO(3) representation of Sec. V C, the average of the quadrupole operator $q_{33}^{(2)}$ over the atomic state defined by two quantum numbers m_1 and m_2, where m_i, $i=1,2$ are the respective eigenvalues for projection of the vector operators $\mathbf{I}^{(i)}$ onto the respective axes $\boldsymbol{\omega}_i$. Let α_i, $i=1,2$ be the angle between vectors $\boldsymbol{\omega}_i$ and **R**, and let β be the angle between vectors $\boldsymbol{\omega}_1$ and $\boldsymbol{\omega}_2$. Algebraic manipulation readily yields the important result

$$\begin{aligned} &\langle m_1m_2|q_{33}^{(2)}|m_1m_2\rangle \\ &= n^2\Big[2m_1^2\cos^2\alpha_1 - 6m_1m_2\cos\alpha_1\cos\alpha_2 + 2m_2^2\cos^2\alpha_2 \\ &\quad + ((n^2-1)/4 - m_1^2)\sin^2\alpha_1 + ((n^2-1)/4 - m_2^2)\sin^2\alpha_2 \\ &\quad - \frac{1}{3}(n^2-1) + 2m_1m_2\cos\beta\Big] \end{aligned}$$

for the quadrupole moment averaged over an algebraic basis set of wave functions with quantum numbers (n,m_1,m_2).

VI. EQUIVALENT OCTUPOLE OPERATOR

The Cartesian components of the octupole moment as a tensor of rank 3 are defined by Eq. (8). The octupolelike combinations of **L** and **A** which have contributions to the equivalent octupole operator within the n-shell are based on $\mathbf{A}\cdot\mathbf{A}\cdot\mathbf{A}$ and $\mathbf{L}\cdot\mathbf{L}\cdot\mathbf{A}$. Other combinations have even parity and are forbidden by the parity rule, as previously explained in Sec. III.

Following our general procedure, we seek the equivalent octupole operators in the form

$$P_n q^{(3)} P_n = aO^{(1)} + bO^{(2)},$$

where the tensor operator $O^{(1)}$ is derived from the set $\mathbf{A}\cdot\mathbf{A}\cdot\mathbf{A}$ and $O^{(2)}$ from the set $\mathbf{L}\cdot\mathbf{L}\cdot\mathbf{A}$, respectively. The precise method for constructing these operators is now explained.

The matrix elements of the 333 tensor components between states with one and three units difference in angular momentum number are compared. The unknown coefficients a and b are then solutions of the set of equations

$$\begin{aligned} &\langle nl-1m|q_{333}^{(3)}|nlm\rangle \\ &\quad = a\langle nl-1m|O_{333}^{(1)}|nlm\rangle + b\langle nl-1m|O_{333}^{(2)}|nlm\rangle, \end{aligned}$$

$$\begin{aligned} &\langle nl-3m|q_{333}^{(3)}|nlm\rangle \\ &\quad = a\langle nl-3m|O_{333}^{(1)}|nlm\rangle + b\langle nl-3m|O_{333}^{(2)}|nlm\rangle. \end{aligned}$$

The Cartesian components $O_{ijk}^{(1)}$ and $O_{ijk}^{(2)}$ of the octupole-like operators are now constructed from $A_iA_jA_k$ and $L_iL_jA_k$, respectively. Three operations are then applied to these elementary combinations to insure that the resulting operators possess the following properties: (1) they have zero trace when any pair of indices are contracted, (2) they are fully symmetric with respect to index permutations, and (3) they

are symmetric over the order of noncommuting factors.

Given three vector operators **a**, **b**, and **c**, the ijk component of the most general octupole-type operator is given by

$$o_{ijk}(\mathbf{a},\mathbf{b},\mathbf{c}) = \mathcal{Z}\left[a_i b_j c_k - \frac{1}{5}\delta_{jk}\sum_{s=1}^{3} a_i b_s c_s - \frac{1}{5}\delta_{ij}\sum_{s=1}^{3} a_s b_s c_k - \frac{1}{5}\delta_{ik}\sum_{s=1}^{3} a_s b_j c_s\right], \tag{21}$$

where $\mathcal{Z}$ represents the operation of symmetrization with respect to *both* index and vector permutations. For example,

$$\mathcal{Z}[a_i b_j c_k] = \frac{1}{36}\sum_{\rho}\sum_{\pi} \rho(a)_{\pi(i)}\rho(b)_{\pi(j)}\rho(c)_{\pi(k)}, \tag{22}$$

where ρ represents a permutation of the vector set $\{a,b,c\}$ and where π is a permutation of the index set $\{i,j,k\}$. It is easy to check that the combination (21) obtained in this way possess all of the above (1)–(3) required properties.

Implementation. According to the general prescription (21) above, the operator (8) takes the form $o_{ijk}=o_{ijk}(\mathbf{r},\mathbf{r},\mathbf{r})$ so that its zzz (or 333) component in Cartesian representation is

$$q^{(3)}_{333} = o_{333}(\mathbf{r},\mathbf{r},\mathbf{r}) = x_3^3 - \frac{3}{5}r^2 x_3,$$

as expected. From vectors **L** and **A**, two octupole operators with the same parity as for o_{ijk} can be constructed. One is $O^{(1)}_{ijk}=o_{ijk}(\mathbf{A},\mathbf{A},\mathbf{A})$ and the other is $O^{(2)}_{ijk}=o_{ijk}(\mathbf{A},\mathbf{L},\mathbf{L})$.

The zzz (or 333) component of the octupole-type operator $O^{(1)}$ is

$$O^{(1)}_{333} = o_{333}(\mathbf{A},\mathbf{A},\mathbf{A}) = \mathcal{Z}\left[A_3^3 - \frac{3}{5}\sum_s (A_s A_s)A_3\right]. \tag{23}$$

With the aid of Eq. (22) and the commutation relations $[A_i,A_j]=i\epsilon_{ijk}L_k$ and $[L_i,A_j]=i\epsilon_{ijk}A_k$, expression (23) reduces eventually (see Appendix B 1) to simply

$$O^{(1)}_{333} = A_3^3 - \frac{3}{10}(A^2A_3 + A_3A^2) + \frac{1}{5}A_3. \tag{24}$$

The second operator

$$O^{(2)}_{333} = o_{333}(\mathbf{L},\mathbf{L},\mathbf{A}) = \mathcal{Z}\left\{L_3^2A_3 - \frac{1}{5}\sum_s [(A_sL_s)L_3 + (L_sA_s)L_3 + (L_sL_s)A_3]\right\}, \tag{25}$$

with the aid of similar algebraic reduction and the additional identity $\mathbf{A}\cdot\mathbf{L}=\mathbf{L}\cdot\mathbf{A}=0$, eventually reduces (see Appendix B 2) to

$$O^{(2)}_{333} = L_3^2A_3 - \frac{1}{10}(L^2A_3 + A_3L^2) + \frac{1}{5}A_3. \tag{26}$$

Using Eqs. (A26)–(A31) of Appendix A, the solution of the set of equations of matrix elements yields the required coefficients to be $a=-\frac{35}{8}n^3$ and $b=\frac{15}{8}n^3$. The equivalent octupole operator within the n shell is therefore

$$P_n q^{(3)}_{ijk} P_n = -\frac{35n^3}{8}o_{ijk}(\mathbf{A},\mathbf{A},\mathbf{A}) + \frac{15n^3}{8}o_{ijk}(\mathbf{L},\mathbf{L},\mathbf{A}). \tag{27}$$

This is our desired rule which replaces the Cartesian octupole (8) by Eq. (27), where the general components o_{ijk} are determined in the prescribed manner.

In particular, the sequences involved are provided in Appendix B for the o_{333} case, as an example characteristic of the overall calculational procedure. Specifically, Eq. (27), with the aid of $A^2+L^2+1=n^2$, yields the expression

$$P_n q^{(3)}_{333} P_n = \frac{5n^3}{8}\left[3L_3^2A_3 + \frac{12}{5}(A^2A_3 + A_3A^2) - 7A_3^2\right] - \frac{n^3}{8}(3n^2+5) \tag{28}$$

for the equivalent octupole 333-component operator in the $(\mathbf{L},\mathbf{A})$ representation.

VII. LIST OF EQUIVALENT MULTIPOLE OPERATORS AND A TEST EXAMPLE

We have shown that the Cartesian dipole, quadrupole, and octupole operators

$$q_i^{(1)} = x_i, \tag{29}$$

$$q_{ij}^{(2)} = x_i x_j - \frac{1}{3}r^2\delta_{ij}, \tag{30}$$

$$q_{ijk}^{(3)} = x_i x_j x_k - \frac{1}{5}r^2(x_i\delta_{jk} + x_j\delta_{ik} + r_k\delta_{ij}) \tag{31}$$

have the equivalent intrashell dipole, quadrupole, and octupole operators

$$q_i^{(1)} = -\frac{3}{2}nA_i, \tag{32}$$

$$q_{ij}^{(2)} = -\frac{n^2}{4}\left(L_iL_j + L_jL_i - \frac{2}{3}L^2\delta_{ij}\right) + \frac{5n^2}{4}\left(A_iA_j + A_jA_i - \frac{2}{3}A^2\delta_{ij}\right), \tag{33}$$

$$q_{ijk}^{(3)} = -\frac{35}{8}n^3O^{(1)}_{ijk} + \frac{15}{8}n^3O^{(2)}_{ijk} \tag{34}$$

expressed explicitly in terms of the **L** and **A** integrals of the motion on the energy shell. Equation (32) reproduces the Pauli [7] operator replacement rule $\mathbf{r}\equiv-(3n/2)\mathbf{A}$, for the dipole Cartesian component (29). Equations (33) and (34) summarize our replacement rules for both the quadrupole and octupole Cartesian elements (30) and (31). The operators $O^{(1)}_{ijk}=o_{ijk}(\mathbf{A},\mathbf{A},\mathbf{A})$ and $O^{(2)}_{ijk}=o_{ijk}(\mathbf{L},\mathbf{L},\mathbf{A})$ are defined in Sec.

VI and are calculated in Appendix B. The n^{λ} scaling law is apparent in Eqs. (32)–(34). Note that equivalent operators generally contain several terms with simple coefficients.

Application: *Multipoles of extreme Stark states*. As a test example, consider the permanent multipole moments associated with the extreme Stark hydrogenic states, i.e., for those Stark (parallel and antiparallel) states most stretched along the positive and negative direction of the Z axis. With the aid of the replacement rules (32)–(34), the appropriate spherical multipole operators $Q_0^{(\lambda)}$ are

$$Q_0^{(1)} = q_3^{(1)} = -\frac{3n}{2}A_3, \tag{35}$$

$$Q_0^{(2)} = \frac{3}{2}q_{33}^{(2)} = -\frac{3n^2}{4}\left(L_3^2 - \frac{1}{3}L^2\right) + \frac{15n^2}{4}\left(A_3^2 - \frac{1}{3}A^2\right), \tag{36}$$

$$Q_0^{(3)} = \frac{5}{2}q_{333}^{(3)} = -\frac{175n^3}{16}\left(A_3^3 + \frac{1}{5}A_3 - \frac{3}{10}A^2A_3 - \frac{3}{10}A_3A^2\right) + \frac{75n^3}{16}\left(L_3^2A_3 + \frac{1}{5}A_3 - \frac{1}{10}L^2A_3 - \frac{1}{10}A_3L^2\right). \tag{37}$$

The parabolic and algebraic representation of these states are, respectively,

$$\psi_{(n-1)00}(\mathbf{r}) \equiv |+\rangle = |n,j,-j\rangle,$$

$$\psi_{0(n-1)0}(\mathbf{r}) \equiv |-\rangle = |n,-j,j\rangle.$$

Any of these hydrogenic stretched states $|\alpha\rangle = |\pm\rangle$ has expectation value

$$Q_0^{(\lambda)} \equiv \langle\alpha|\mathrm{Q}_\mu^{(\lambda)}|\alpha\rangle = \langle\alpha|\mathrm{Q}_0^{(\lambda)}|\alpha\rangle\delta_{\mu 0}. \tag{38}$$

For the "plus" states $|+\rangle = |n,j,-j\rangle$ of the algebraic basis, we have

$$Q_0^{(1)}(+) = \langle + |Q_0^{(1)}| + \rangle = -\frac{3n}{2}A_3(+),$$

where $A_3(+) = -2j = -(n-1)$, so that

$$Q_0^{(1)}(+) = \frac{3n(n-1)}{2}$$

is the permanent dipole moment for the extreme stretched Stark state. On using $L_3(+)=0$, $L^2(+)=n-1$, and $A^2(+)=n(n-1)$, the quadrupole and octupole moments are

$$Q_0^{(2)}(+) = \frac{1}{2}n^2(n-1)(5n-7)$$

and

$$Q_0^{(3)}(+) = \frac{5}{8}n^3(n-1)(n-2)(7n-9),$$

respectively. All these moments are in exact agreement with the analytical results [8] of theory recently developed solely for the case of these extreme Stark states. Matrix elements of operators (35)–(37) over the (n, l, m) basis have also been checked for $n=1-6$.

VIII. CONCLUSIONS

We have shown that it is possible to construct both the quadrupole and octopole operators solely in terms of the $\mathbf{A},\mathbf{L}$ operators which are integrals of motion on the energy shell with quantum number n. We have provided and illustrated the various steps involved with their construction and have derived explicit expressions for these operators. The basic importance of these expressions is that they furnish the ability to solve various structure and collision problems solely by algebraic group theoretical techniques and commutation relations based on the SO(4) symmetry of the hydrogen atom, when the dynamics is confined to the energy shell. We gave various useful averages of these operators. Our general theory readily provides the permanent dipole, quadrupole, and octupole of polar Rydberg atoms in their extreme Stark states, a case which can be also solved by less-sophisticated standard techniques. The present treatment will be key to further developments in the theory of Stark l mixing via the combined charge-dipole, charge-quadrupole, and charge-octupole interactions evident in ion-Rydberg atom collisions. The present study would also be important to investigation [14,15] of Rydberg atoms in the field of electric multipoles.

Although the dipole, quadrupole, and octupole are the most significant in many practical applications, the full general solution for any multipole remains, at present, elusive. Although plausible, the very existence of equivalent operators for a general multipole is not completely certain. Consider, for instance, the hexadecapole operator [i.e., Eq. (5) with $\lambda=4$]. Here three tensor operators are appropriate: $O^{(1)}$ derived from the set $\mathbf{A}\cdot\mathbf{A}\cdot\mathbf{A}\cdot\mathbf{A}$, $O^{(2)}$ derived from the set $\mathbf{A}\cdot\mathbf{A}\cdot\mathbf{L}\cdot\mathbf{L}$, and $O^{(3)}$ derived from the set $\mathbf{L}\cdot\mathbf{L}\cdot\mathbf{L}\cdot\mathbf{L}$, while the sets $\mathbf{A}\cdot\mathbf{A}\cdot\mathbf{A}\cdot\mathbf{L}$ and $\mathbf{A}\cdot\mathbf{L}\cdot\mathbf{L}\cdot\mathbf{L}$ with odd-parity are all forbidden. The equivalent operator can then be taken as the linear combination $aO^{(1)}+bO^{(2)}+cO^{(3)}$. Three nonzero nondiagonal intrashell matrix elements ($l'=l$, $l'=l-2$, and $l'=l-4$) are then used to fit the coefficients a,b,c, in the manner prescribed in Sec. VI.

Although this reasoning could, in principle, be extended to higher multipoles, the overall procedure ultimately becomes quite cumbersome for actual calculations for larger λ. The simplicity of the coefficients in formulas (32)–(34) possibly indicates that there may well be simpler methods of derivation. Although fruitful, the present theoretical systematic pole-by-pole approach may not be sufficiently powerful for the general multipole case. Instead, some other more encompassing approach, probably based on study of commutation relations (similar in spirit to the derivation of Pauli replacement rule in the Appendix of Ref. [3]) could be developed.

Finally, we indicate that there is another context where equivalent operators are of key importance. Namely, higher order contributions from external fields might be expressed in terms of equivalent operators. These effects imply virtual intershell (n-changing) transitions conveniently expressed

via Green functions. Although equivalent operators were constructed quite long ago by Solov'ev [12] for the second-order contributions from electric fields, higher orders have, as yet, not been considered. Equivalent operators of this type are beyond the scope of the present study.

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APPENDIX A: INTRASHELL MATRIX ELEMENTS

1. Radial and angular elements

A general expression for intrashell radial matrix elements of integer power of r is (see Ref. [16], for example)

$$\begin{aligned}(nl'|r^{\beta}|nl) &= \int_0^{\infty} R_{nl'}(r)R_{nl}(r)r^{\beta+2}dr \\ &= \frac{1}{4}\left(\frac{n}{2}\right)^{\beta-1}\left[\frac{(n+l_>)!(n-l_>-1)!}{(n+l_<)!(n-l_<-1)!}\right]^{1/2}(-1)^{l_>+l_<+\beta+1} \\ &\quad\times\sum_{i=i_0}^{\beta+1}\frac{(-1)^i}{i!(\beta+1-i)!} \\ &\quad\times\frac{(n+l_<+i)!(n-l_<-1+i)!}{[n+l_>+i-(\beta+1)]![n-l_>-1+i-(\beta+1)]!},\end{aligned}$$

where the lower limit in summation is $i_0=\max[0,\beta+1-(n-l_>-1)]$, $l_>=\max(l,l')$, and $l_<=\min(l,l')$. This general equation yields the following useful matrix elements for low powers of r:

$$(nl|r^0|nl) = 1, \tag{A1}$$

$$(nl|r^1|nl) = \frac{1}{2}[3n^2 - l(l+1)], \tag{A2}$$

$$(nl-1|r^1|nl) = -\frac{3}{2}n\sqrt{n^2-l^2}, \tag{A3}$$

$$(nl|r^2|nl) = \frac{1}{2}n^2[5n^2 - 3l(l+1) + 1], \tag{A4}$$

$$(nl-1|r^2|nl) = -\frac{1}{2}n(5n^2 - l^2 + 1)\sqrt{n^2-l^2}, \tag{A5}$$

$$(nl-2|r^2|nl) = \frac{5}{2}n^2\sqrt{[n^2-l^2][n^2-(l-1)^2]}, \tag{A6}$$

$$(nl|r^3|nl) = \frac{1}{8}n^2\{35n^4 - 5n^2[6l(l+1)-5] + 3l(l-1)(l+1)(l+2)\}, \tag{A7}$$

$$(nl-1|r^3|nl) = -\frac{5}{8}n^3(7n^2 - 3l^2 + 5)\sqrt{n^2-l^2}, \tag{A8}$$

$$(nl-2|r^3|nl) = \frac{5}{8}n^2[7n^2 - l(l-1) + 2] \times\sqrt{[n^2-l^2][n^2-(l-1)^2]}, \tag{A9}$$

$$(nl-3|r^3|nl) = -\frac{35}{8}n^3\sqrt{[n^2-l^2][n^2-(l-1)^2][n^2-(l-2)^2]}. \tag{A10}$$

The standard angular integral is

$$\begin{aligned}(l_3m_3|Y_{l_2m_2}|l_1m_1) &= \int d\Omega Y_{l_1m_1}(\Omega)Y_{l_2m_2}(\Omega)Y_{l_3m_3}(\Omega)^* \\ &= \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l_3+1)}}C^{l_30}_{l_10l_20}C^{l_3m_3}_{l_1m_1l_2m_2}.\end{aligned}$$

From standard tables (see Ref. [9], for example) of the Clebsch-Gordan coefficients $C^{l_3m_3}_{l_1m_1l_2m_2}$, we obtain the following angular integrals for the quantum numbers of interest:

$$(l-1m|Y_{10}|lm) = \sqrt{\frac{3}{4\pi}}\sqrt{\frac{l^2-m^2}{(2l-1)(2l+1)}}, \tag{A11}$$

$$(lm|Y_{20}|lm) = \sqrt{\frac{5}{4\pi}}\frac{l(l+1)-3m^2}{(2l-1)(2l+3)}, \tag{A12}$$

$$(l-2m|Y_{20}|lm) = \sqrt{\frac{5}{4\pi}}\frac{3}{4(2l-1)}\sqrt{\frac{(l^2-m^2)[(l-1)^2-m^2]}{(2l-3)(2l+1)}}, \tag{A13}$$

$$(l-1m|Y_{30}|lm) = \sqrt{\frac{7}{4\pi}}\frac{3}{2}\frac{l^2-5m^2-1}{(2l-3)(2l+3)}\sqrt{\frac{l^2-m^2}{(2l-1)(2l+1)}}, \tag{A14}$$

$$(l-3m|Y_{30}|lm) = \sqrt{\frac{7}{4\pi}}\frac{5}{2(2l-3)(2l-1)} \times\sqrt{\frac{(l^2-m^2)[(l-1)^2-m^2][(l-2)^2-m^2]}{(2l-5)(2l+1)}}. \tag{A15}$$

2. Dipole matrix elements for Sec. IV

On using the relation (9), radial (A3), and angular (A11) integrals, the dipole matrix elements are

$$\langle nl-1m|q_3^{(1)}|nlm\rangle = \langle nl-1m|Q_0^{(1)}|nlm\rangle = \sqrt{\frac{4\pi}{3}}(nl-1|r|nl)(l-1m|Y_{10}|lm) = -\frac{3n}{2}\sqrt{\frac{(n^2-l^2)(l^2-m^2)}{(2l-1)(2l+1)}}. \quad \text{(A16)}$$

3. *A* and *L* operators

The action of Runge-Lenz vector on n-shell states is (see Adams [1], p. 112, DeLange and Raab [1], p. 264, or Ref. [17], for example)

$$A_3|nlm\rangle = \sqrt{\frac{(n^2-l^2)(l^2-m^2)}{(2l-1)(2l+1)}}|nl-1m\rangle + \sqrt{\frac{[n^2-(l+1)^2][(l+1)^2-m^2]}{(2l+1)(2l+3)}}|nl+1m\rangle. \quad \text{(A17)}$$

The Pauli replacement rule $\mathbf{r}\to-(3n/2)\mathbf{A}$ immediately follows on comparing Eqs. (A16) and (A17).

In terms of the coefficient

$$g_{nl} = \sqrt{\frac{(n^2-l^2)(l^2-m^2)}{(2l-1)(2l+1)}}, \quad \text{(A18)}$$

Eq. (A17) can be rewritten as the linear combination

$$A_3|nlm\rangle = g_{nl}|nl-1m\rangle + g_{nl+1}|nl+1m\rangle \quad \text{(A19)}$$

of $(n,l\pm1,m)$ states. The operators $A_\pm=A_1\pm iA_2$ which change m by ±1, respectively, can also be written as the similar combinations

$$A_+|nlm\rangle = +\beta_{m,l-1}c_{nl}|nl-1m+1\rangle - \gamma_{m,l+1}c_{nl+1}|nl+1m+1\rangle,$$

$$A_-|nlm\rangle = -\beta_{-m,l-1}c_{nl}|nl-1m-1\rangle + \gamma_{-m,l+1}c_{nl+1}|nl+1m-1\rangle$$

of $(n,l\pm1,m\pm1)$ states. The coefficients are

$$\beta_{m,l} = \sqrt{(l-m+1)(l-m)},$$

$$\gamma_{m,l} = \sqrt{(l+m+1)(l+m)},$$

$$c_{nl} = \sqrt{(n^2-l^2)/(2l-1)(2l+1)}.$$

For completeness with above, the components L_3 and $L_\pm=L_1\pm iL_2$ of the $\mathbf{L}$ operator obey the standard relations

$$L_3|nlm\rangle = m|nlm\rangle,$$

$$L_+|nlm\rangle = \omega_{m,l}|nlm+1\rangle,$$

$$L_-|nlm\rangle = \omega_{-m,l}|nlm-1\rangle,$$

where $\omega_{m,l}=\sqrt{(l-m)(l+m+1)}$.

In the subsequent reduction of the basic A_iA_j and L_iL_j operations within the quadrupole operators $O_{ij}^{(1)}$ and $O_{ij}^{(2)}$ and the $A_iA_jA_k$, $A_iL_jL_k$, and $L_iL_jA_k$ operations within the octupole operators $O_{ijk}^{(1)}$ and $O_{ijk}^{(2)}$, frequent use is made of the standard commutation relations $[A_i,A_j]=i\epsilon_{ijk}L_k$, and $[L_i,L_j]=i\epsilon_{ijk}L_k$ together with $[L_i,A_j]=i\epsilon_{ijk}A_k$ (which relation rotates A_j about axis i to give A_k, thereby confirming the vector character of $\mathbf{A}$). We also employ the additional relations $\Sigma_sA_sL_s\equiv(\mathbf{A}\cdot\mathbf{L})=0$ and $\Sigma_sL_sA_s\equiv(\mathbf{L}\cdot\mathbf{A})=0$ for $O_{333}^{(2)}$ reduction.

4. Quadrupole matrix elements for Sec. V

On using the relation (10), radial (A4), and angular (A12) integrals, the quadrupole matrix elements are

$$\langle nlm|q_{33}^{(2)}|nlm\rangle = \frac{2}{3}\langle nlm|Q_0^{(2)}|nlm\rangle = \frac{2}{3}\sqrt{\frac{4\pi}{5}}(nl|r^2|nl)(lm|Y_{20}|lm) = \frac{n^2}{3}\frac{l(l+1)-3m^2}{(2l-1)(2l+3)}(5n^2-3l^2-3l+1) \quad \text{(A20)}$$

and similarly, using Eqs. (A6) and (A13),

$$\langle nl-2m|q_{33}^{(2)}|nlm\rangle = \frac{2}{3}\langle nl-2m|Q_0^{(2)}|nlm\rangle = \frac{2}{3}\sqrt{\frac{4\pi}{5}}(nl-2|r^2|nl)(l-2m|Y_{20}|lm) = \frac{5n^2}{2(2l-1)} \times\sqrt{\frac{(n^2-l^2)[n^2-(l-1)^2](l^2-m^2)[(l-1)^2-m^2]}{(2l-3)(2l+1)}}. \quad \text{(A21)}$$

On using Eq. (A19), direct algebraic calculation of the matrix elements of the quadrupole operators (14) and (15) yields

$$\langle nlm|O_{33}^{(1)}|nlm\rangle = g_{nl}^2 + g_{nl+1}^2 - \frac{1}{3}[n^2-l(l+1)-1], \quad \text{(A22)}$$

$$\langle nl-2m|O_{33}^{(1)}|nlm\rangle = g_{nl}g_{nl-1}, \quad \text{(A23)}$$

$$\langle nlm|O_{33}^{(2)}|nlm\rangle = -\frac{1}{3}[l(l+1)-3m^2], \quad \text{(A24)}$$

$$\langle nl-2m|O_{33}^{(2)}|nlm\rangle = 0, \quad \text{(A25)}$$

in terms of the g_{nl} coefficient (A18). The relation $A^2+L^2=n^2-1$ has been used for Eq. (A22).

5. Octupole matrix elements for Sec. VI

The octupole matrix elements calculated using Eqs. (11), (A8), (A10), (A14), and (A15) are

$$\langle nl-1m|q_{333}^{(3)}|nlm\rangle = \frac{2}{5}\sqrt{\frac{4\pi}{7}}(nl-1|r^3|nl)(l-1m|Y_{30}|lm)$$
$$= -\frac{3n^3}{8}\frac{(7n^2-3l^2+5)(l^2-5m^2-1)}{(2l-3)(2l+3)}\sqrt{\frac{(n^2-l^2)(l^2-m^2)}{(2l-1)(2l+1)}} \tag{A26}$$

and

$$\langle nl-3m|q_{333}^{(3)}|nlm\rangle = \frac{2}{5}\sqrt{\frac{4\pi}{7}}(nl-3|r^3|nl)(l-3m|Y_{30}|lm)$$
$$= -\frac{35n^3}{8(2l-3)(2l-1)}\sqrt{\frac{(n^2-l^2)[n^2-(l-1)^2][n^2-(l-2)^2](l^2-m^2)[(l-1)^2-m^2][(l-2)^2-m^2]}{(2l-5)(2l+1)}}. \tag{A27}$$

Direct calculation based on Eq. (A19) then provides the following octupole matrix elements:

$$\langle nl-1m|O_{333}^{(1)}|nlm\rangle = g_{nl}\left[g_{nl-1}^2+g_{nl}^2+g_{nl+1}^2+\frac{1}{5}-\frac{3}{5}(n^2-l^2-1)\right], \tag{A28}$$

$$\langle nl-3m|O_{333}^{(1)}|nlm\rangle = g_{nl}g_{nl-1}g_{nl-2}, \tag{A29}$$

$$\langle nl-1m|O_{333}^{(2)}|nlm\rangle = -\frac{1}{5}g_{nl}(l^2-5m^2-1), \tag{A30}$$

$$\langle nl-3m|O_{333}^{(2)}|nlm\rangle = 0, \tag{A31}$$

in terms of the coefficient (A18). The relation $A^2+L^2=n^2-1$ has been used in Eq. (A28).

APPENDIX B: (A,L) Representation for operators $O_{333}^{(1)}$ and $O_{333}^{(2)}$

We illustrate here the procedure for evaluating, in terms of $(\mathbf{A},\mathbf{L})$, the $O_{333}^{(1)}$ and $O_{333}^{(2)}$ operators from their basic definitions (23) and (25). At the outset, proper account must be taken of the inherent $\mathcal{Z}$-operation prescribed by formula (22) for symmetrization with respect to *both* index and vector permutations.

1. The $O_{333}^{(1)}$ component

The definition of $O_{333}^{(1)}$ is

$$O_{333}^{(1)} = o_{333}(\mathbf{A},\mathbf{A},\mathbf{A}) = \mathcal{Z}\left[A_3^3-\frac{3}{5}\sum_s (A_sA_s)A_3\right]. \tag{B1}$$

The first term $\mathcal{Z}A_3^3=A_3^3$ is left unaffected. The symmetrized sum can be evaluated via the following progression of steps:

$$\mathcal{Z}\sum_s (A_sA_s)A_3 = \frac{1}{6}\sum_s (A_sA_sA_3+A_sA_3A_s+A_sA_sA_3+A_sA_3A_s+A_3A_sA_s+A_3A_sA_s)$$
$$= \frac{1}{3}(A^2A_3+A_3A^2)+\frac{1}{3}\sum_s A_sA_3A_s$$
$$= \frac{1}{3}(A^2A_3+A_3A^2)+\frac{1}{6}\sum_s (A_sA_sA_3-A_sA_sA_3+2A_sA_3A_s-A_3A_sA_s+A_3A_sA_s)$$
$$= \frac{1}{2}(A^2A_3+A_3A^2)+\frac{1}{6}\sum_s (A_s[A_3,A_s]-[A_3,A_s]A_s)$$
$$= \frac{1}{2}(A^2A_3+A_3A^2)+\frac{1}{6}[A_1iL_2-iL_2A_1+A_2(-iL_1)-(-iL_1)A_2]$$
$$= \frac{1}{2}(A^2A_3+A_3A^2)+\frac{1}{6}i([A_1,L_2]-[A_2,L_1])$$
$$= \frac{1}{2}(A^2A_3+A_3A^2)+\frac{1}{6}i(iA_3+iA_3)$$
$$= \frac{1}{2}(A^2A_3+A_3A^2)-\frac{1}{3}A_3.$$

The $O_{333}^{(1)}$ operator (B1) therefore reduces to

$$O_{333}^{(1)} = A_3^3-\frac{3}{10}(A^2A_3+A_3A^2)+\frac{1}{5}A_3 \tag{B2}$$

as stated by Eq. (24) of the text.

2. The $O_{333}^{(2)}$ component

$O_{333}^{(2)}$ is defined by

$$O_{333}^{(2)} = o_{333}(\mathbf{L},\mathbf{L},\mathbf{A}) = \mathcal{Z}\left\{ L_3^2 A_3 - \frac{1}{5}\sum_s [(A_s L_s)L_3 + (L_s A_s)L_3 + (L_s L_s)A_3] \right\}. \tag{B3}$$

Because the operators L_3 and A_3 commute, the first term $\mathcal{Z}L_3^2 A_3 = L_3^2 A_3$ is left unaffected. Symmetrization of the remaining terms proceeds via the following steps:

$$\begin{aligned}
\mathcal{Z}\sum_s [(A_s L_s)L_3 + (L_s A_s)L_3 + (L_s L_s)A_3] &= \frac{1}{6}\sum_s (A_s L_s L_3 + A_s L_3 L_s + L_s A_s L_3 + L_s L_3 A_s + L_3 A_s L_s + L_3 L_s A_s + L_s A_s L_3 + L_s L_3 A_s + A_s L_s L_3 \\
&\quad + A_s L_3 L_s + L_3 L_s A_s + L_3 A_s L_s + L_s L_s A_3 + L_s A_3 L_s + L_s L_s A_3 + L_s A_3 L_s + A_3 L_s L_s + A_3 L_s L_s) \\
&= \frac{1}{3}\sum_s (A_s L_s L_3 + A_s L_3 L_s + L_s A_s L_3 + L_s L_3 A_s + L_3 A_s L_s + L_3 L_s A_s) + \frac{1}{3}(L^2 A_3 + A_3 L^2) \\
&\quad + \frac{1}{3}\sum_s L_s A_3 L_s = \frac{1}{3}\sum_s (A_s L_3 L_s + L_s L_3 A_s) + \frac{1}{3}(L^2 A_3 + A_3 L^2) + \frac{1}{3}\sum_s L_s A_3 L_s.
\end{aligned} \tag{B4}$$

The first sum on the right-hand side of (B4) transforms from

$$\begin{aligned}
S_1 &\equiv \sum_s (A_s L_3 L_s + L_s L_3 A_s) \\
&= \sum_s (A_s L_3 L_s - A_s L_s L_3 + L_s L_3 A_s - L_3 L_s A_s) \\
&= \sum_s (A_s [L_3, L_s] - [L_3, L_s] A_s)
\end{aligned}$$

to

$$\begin{aligned}
S_1 &= A_1 i L_2 - i L_2 A_1 + A_2(-i)L_1 - (-i)L_1 A_2 \\
&= i[A_1, L_2] - i[A_2, L_1] = -2A_3.
\end{aligned}$$

The second sum on the right-hand side of (B4) becomes reduced by the steps from

$$\begin{aligned}
S_2 &\equiv \sum_s L_s A_3 L_s \\
&= \frac{1}{2}\sum_s (L_s L_s A_3 - L_s L_s A_3 + 2L_s A_3 L_s + A_3 L_s L_s - A_3 L_s L_s) \\
&= \frac{1}{2}(L^2 A_3 + A_3 L^2) + \frac{1}{2}\sum_s (L_s [A_3, L_s] - [A_3, L_s] L_s) \\
&= \frac{1}{2}(L^2 A_3 + A_3 L^2) + \frac{1}{2}(L_1 i A_2 - i A_2 L_1 - L_2 i A_1 + i A_1 L_2) \\
&= \frac{1}{2}(L^2 A_3 + A_3 L^2) + \frac{1}{2}(i[L_1, A_2] - i[L_2, A_1]) \\
&= \frac{1}{2}(L^2 A_3 + A_3 L^2) + \frac{1}{2}(i i A_3 + (-i)(-i) i A_3)
\end{aligned} \tag{B5}$$

to

$$S_2 = \frac{1}{2}(L^2 A_3 + A_3 L^2) - A_3.$$

The full $O_{333}^{(2)}$ operator (B3) is therefore

$$O_{333}^{(2)} = L_3^2 A_3 - \frac{1}{10}(L^2 A_3 + A_3 L^2) + \frac{1}{5}A_3, \tag{B6}$$

as stated by Eq. (26) of the text. The end term of Eq. (B6) being extracted from the detailed algebraic calculation above, is the least obvious.

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